

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

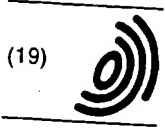
Defects in the images may include (but are not limited to):

① **BLACK BORDERS**

- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 747 403 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
01.09.1999 Bulletin 1999/35

(51) Int Cl.⁶: **C08F 10/00, C08F 4/613**

(21) Application number: **96109109.7**

(22) Date of filing: **07.06.1996**

(54) **A process for producing an isotactic/syndiotactic polymer blend in a single reactor**
Verfahren zur Herstellung einer isotaktischen/syndiotaktischen Polymermischung in einem einzigen Reaktor
Procédé de production d'un mélange de polymère isotactique/syndiotactique dans un seul réacteur

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(30) Priority: **07.06.1995 US 473680**

(43) Date of publication of application:
11.12.1996 Bulletin 1996/50

(73) Proprietor: **FINA TECHNOLOGY, INC.**
Plano, Texas 75024 (US)

(72) Inventors:
• **Reddy, Balreddy R.**
Baytown, Texas 77520 (US)

• **Shamshoum, Edwar S.**
Houston, Texas 77062 (US)

(74) Representative: **Leyder, Francis et al**
c/o Fina Research S.A.
Zone Industrielle C
7181 Feluy (BE)

(56) References cited:
WO-A-95/13871
US-A- 4 659 685 **WO-A-96/01855**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 747 403 B1

Description

BACKGROUND OF THE INVENTION5 FIELD OF THE INVENTION:

[0001] This invention relates to a process for producing polymer blends from a single reactor, specifically a process for producing polymer blends of isotactic polyolefins and syndiotactic polyolefins using a catalyst system which is a combination of at least one metallocene catalyst and at least one conventional supported Ziegler-Natta catalyst.

10 DESCRIPTION OF THE PRIOR ART:

[0002] It is known that two or more homogeneous catalysts, such as those based on metallocene compounds, may be combined to effect properties, such as molecular weight distribution. U.S. Patent No. 4,530,914 discloses use of a catalyst system comprising two or more metallocenes in the polymerization of α -olefins, primarily ethylene, to obtain a broad molecular weight distribution. The metallocenes each have different propagation and termination rate constants. The metallocenes are mixed with an alumoxane to form the catalyst system.

[0003] It is also known that metallocenes may be affixed to a support to simulate a heterogeneous catalyst. In U.S. Patent No. 4,808,561 discloses reacting a metallocene with an alumoxane and forming a reaction product in the presence of a support. The support is a porous material like talc, inorganic oxides such as Group IIA, IIIA IVA OR IVB metal oxides like silica, alumina, silica-alumina, magnesia, titania, zirconia and mixtures thereof, and resinous material such as polyolefins like finely divided polyethylene. The metallocenes and alumoxanes are deposited on the dehydrated support material.

[0004] In U.S. Patent No. 4,701,432 a support is treated with at least one metallocene and at least one non-metallocene transition metal compound. To form a catalyst system a cocatalyst comprising an alumoxane and an organometallic compound of Group IA, IIA, IIB and IIIA is added to the supported metallocene/non-metallocene. The support is a porous solid such as talc or inorganic oxides or resinous materials, preferably an inorganic oxide, such as silica, alumina, silica-alumina, magnesia, titania or zirconia, in finely divided form. By depositing the soluble metallocene on the support material it is converted to a heterogeneous supported catalyst. The transition metal compound, such as $TiCl_4$, is contacted with the support material prior to, after, simultaneously with or separately from contacting the metallocene with the support.

[0005] An advantage of a homogeneous metallocene catalyst system is the very high activity of the catalyst and the narrow molecular weight distribution of the polymer produced with a metallocene catalyst system. The metallocene catalysts suffer from a disadvantage in that the ratio of alumoxane cocatalyst to metallocene is high, requiring extensive treatment of the polymer product to remove the aluminum. Another disadvantage of the homogeneous catalyst system is that the reactor fouls during polymerization.

[0006] It would be advantageous to provide a process to produce a polymer blend of isotactic and syndiotactic polyolefins using a catalyst system of a combination of a homogeneous catalyst with a heterogeneous catalyst in a single reactor.

[0007] A more complete appreciation of the invention and many of the attendant advantages thereof will be readily understood by reference to the following detailed description when considered in connection with the accompanying drawings.

[0008] Figure 1 is a graph of Differential Scanning Calorimetry results from Example 1.

[0009] Figure 2 is a graph of Gel Permeation Chromatography results from Example 2.

[0010] Figure 3 is a graph of Gel Permeation Chromatography results from Example 1.

[0011] Figure 4 is a graph of ^{13}C NMR results from Example 1.

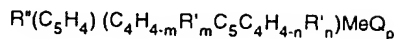
50 SUMMARY OF THE INVENTION

[0012] Accordingly, this invention provides a process and a catalyst system to produce a polymer blend of isotactic polyolefins and syndiotactic polyolefins in a single reactor.

[0013] Also, this invention provides a process and a catalyst system which eliminates reactor fouling during polymerization.

55 [0014] These and other objects are accomplished by: a catalyst system for the polymerization of olefins comprising a combination of at least one homogeneous syndiospecific metallocene catalyst and at least one heterogeneous conventional supported Ziegler-Natta catalyst for producing isotactic polyolefin, wherein the metallocene catalyst comprises:

a) a neutral metallocene compound of the general formula



wherein (C_5H_4) is a cyclopentadienyl ring and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ is a fluorenyl ring or a substituted fluorenyl ring wherein (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R^* is a structural bridge between the (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ rings to impart stereorigidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $0 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

b) an aluminoxane,

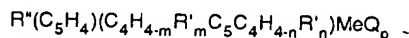
wherein the conventional supported Ziegler-Natta catalyst comprises:

- a) a transition metal compound of the general formula MR^+_x where M is a Group IIIB, IVB, VB or VIB metal, R^+ is a halogen or a hydrocarboxyl and x is the valence of the metal and
- b) an aluminum alkyl of the general formula AlR^*_3 where R^* is an alkyl of from 1-8 carbon atoms and R^* may be the same or different.

[0015] The invention further relates to a method of making a catalyst system comprising

a) making a homogeneous syndiospecific metallocene catalyst by mixing

1) a neutral metallocene compound of the general formula



wherein (C_5H_4) is a cyclopentadienyl ring and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ is a fluorenyl ring or a substituted fluorenyl ring wherein (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R^* is a structural bridge between the (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ rings to impart stereorigidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $1 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

2) an aluminoxane,

b) extracting solvent to form a solid complex of the metallocene and the aluminoxane,

c) suspending the solid in mineral oil,

d) making a heterogeneous conventional supported Ziegler-Natta catalyst by separately mixing:

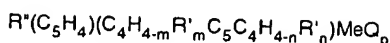
- 1) a conventional supported Ziegler-Natta catalyst component comprising a transition metal compound of the general formula MR^+_x where M is a Group IIIB, IVB, VB or VIB metal, R^+ is a halogen or a hydrocarboxyl and x is the valence of the metal and
- 2) an aluminum alkyl of the general formula AlR^*_3 where R^* is an alkyl of from 1-8 carbon atoms and R^* may be the same or different,

e) mixing the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst.

[0016] According to a further embodiment the invention relates to a process of producing a polymer blend in a single reactor comprising:

a) making a homogeneous syndiospecific metallocene catalyst by

1) selecting a neutral metallocene compound of the general formula



wherein (C_5H_4) is a cyclopentadienyl ring and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ is a fluorenyl ring or a substituted fluorenyl ring wherein (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R^* is a structural bridge between the (C_5H_4) and $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ rings to impart stereorrigidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $1 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

- 2) adding an aluminoxane to form a syndiospecific metallocene catalyst,
- 3) extracting solvent to form a solid complex of the metallocene and the aluminoxane,
- 4) suspending the solid in mineral oil,

b) making a heterogeneous conventional supported Ziegler-Natta catalyst by

- 1) selecting a transition metal compound of the general formula MR^+_x where M is a Group IIIB, IVB, VB or VIB metal, R^+ is a halogen or a hydrocarboxyl and x is the valence of the metal and
- 2) adding an aluminum alkyl of the general formula AlR^*_3 where R^* is an alkyl of from 1-8 carbon atoms and R^* may be the same or different to form a conventional supported Ziegler-Natta catalyst

- c) mixing the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst,
- d) introducing the mixture of the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst into a polymerization reaction zone containing a monomer under polymerization conditions, and
- e) withdrawing a polymer product, which is a blend of syndiotactic and isotactic polyolefins.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention utilizes a multi-catalyst system in the polymerization of any polymer in which separate polymerizations with a homogeneous catalyst and with a heterogeneous catalyst are possible. The multi-catalyst system is useful in the polymerization of olefins, more preferably, α -olefins, and, most preferably, propylene. A Ziegler-Natta catalyst system is disclosed in US-A-5 254 517.

[0018] The multi-catalyst system of the present invention is obtained by mixing the components of at least one metallocene catalyst and at least one conventional supported Ziegler-Natta catalyst. Generally, the components of a metallocene catalyst are a metallocene compound and an ionizing agent. Generally, the components of a conventional supported Ziegler-Natta catalyst are an aluminum alkyl and a transition metal compound with, optionally, an electron donor.

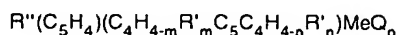
[0019] Any of the conventional heterogeneous Ziegler-Natta transition metal compound catalyst components for producing isotactic polyolefins can be used in the present invention. The compound is of the general formula MR^+_x where M is the metal, R^+ is a halogen or a hydrocarboxyl and x is the valence of the metal. Preferably, M is a Group IVB, VB or VIB metal, more preferably a Group IVB, and most preferably titanium. Preferably, R^+ is chlorine, bromine, an alkoxy or a phenoxy, more preferably chlorine or ethoxy and most preferably, chlorine. Illustrative examples of the transition metal compound catalyst components are $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ and $Ti(OC_{12}H_{25})Cl_3$. Mixtures of the transition metal compounds may be used. No restriction on the number of transition metal compounds is made as long as at least one transition metal compound is present.

[0020] The transition metal compound is supported on an inert solid which is chemically unreactive with any of the components of the heterogeneous or homogeneous catalyst. The support is preferably a magnesium compound. Examples of the magnesium compounds which are to be used to provide a support source for the catalyst component are magnesium halides, dialkoxymagnesiums, alkoxy magnesium halides, magnesium oxyhalides, dialkylmagnesiums, magnesium oxide, magnesium hydroxide, and carboxylates of magnesium.

[0021] The aluminum alkyl is of the general formula AlR^*_3 where R^* is an alkyl of from 1-8 carbon atoms and R^* may be the same or different. Examples of aluminum alkyls are trimethyl aluminum (TMA), triethyl aluminum (TEAL) and triisobutyl aluminum (TiBAI). The preferred aluminum alkyl is TEAL.

[0022] The electron donor is any one of the electron donors which are effective with conventional supported Ziegler-Natta catalysts. Typically, an electron donor is an organosilicon compound. Examples of electron donors are cyclohexylmethyldimethoxysilane (CMDs), diphenyldimethoxy silane (DPMS) and isobutyltrimethoxy silane (IBMS). Other examples of electron donors are disclosed in U.S. Patent Nos. 4,218,339; 4,395,360; 4,328,122; 4,473,660; 4,562,173 and 4,547,552.

[0023] The metallocene catalyst is formed from a neutral metallocene compound, i.e., a metal derivative of a cyclopentadiene. The metallocene compound useful in the present invention contains two cyclopentadiene rings and is of the general formula:



wherein (C_5H_4) is a cyclopentadienyl ring and $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ is a fluorenyl ring or a substituted fluorenyl ring, the substituent preferably being alkyl, alkoxy, dialkylamino, halogens, cycloalkyl or aryl; R' is a hydrocarbyl radical, halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical having from 1-20 carbon atoms, each R' may be the same or different; R'' is a structural bridge between the (C_5H_4) and $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ rings to impart stereoregidity and, preferably, is an alkylene radical having 1-4 carbon atoms, or arylalkyl or diaryl alkyl radical contains 7-20 atoms, a silicon hydrocarbyl compound, a germanium hydrocarbyl compound, an alkyl phosphine, or an alkyl amine; Q is a hydrocarbon radical, such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having 1-20 carbon atoms, or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $0 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

[0024] The cyclopentadienyl rings (C_5H_4) and $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ must have bilateral or pseudo-bilateral symmetry. Bilateral symmetry is defined as the condition in which there is no substituents or one or more substituents on one side and no substituents or one or more substituents on the other side in the same relative position such that a mirror image is formed from one side to another. Pseudobilateral symmetry is defined as symmetry such that a mirror image exists from one side to the other in regard to the existence and position of substituents but the substituents themselves are not identical.

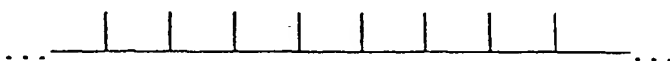
[0025] The metallocene catalyst is syndiotactic specific or syndiospecific. Such catalyst are described in U.S. Patents Nos. 4,895,851; 5,162,278; 5,155,080; 5,132,381 and European Patent Application Publication Nos. 0 387 609; 0 387 690; 0 387 691; and PCT International Publication No. WO 92/1218.

[0026] The ionizing agent is an alumoxane, an aluminum alkyl, other Lewis acid or a combination thereof which will ionize a neutral metallocene compound to form a cationic metallocene catalyst. An examples of an ionizing agents useful in the present invention is methyl alumoxane (MAO).

[0027] The metallocene catalyst is provided in solid form as a complex of the metallocene catalyst component and MAO.

[0028] Olefins, especially propylene, may be polymerized to form polyolefins in amorphous (atactic) or crystalline forms. Examples of crystalline forms are isotactic and syndiotactic.

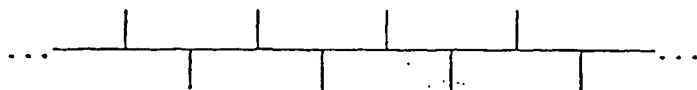
[0029] Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



The methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer, e.g., the methyl groups are all above or below the plane.

[0030] Another way of describing the structure is through the use of NMR. Bovey's NMR nomenclature for an isotactic pentad is ...mmmm... with each "m" representing a "meso" dyad or successive methyl groups on the same side in the plane. As known in the art, any deviation or inversion in the structure of the chain lowers the degree of isotacticity and crystallinity of the polymer.

[0031] A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:



The methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer.

[0032] In NMR nomenclature, this pentad is described as ...rrrr... in which each "r" represents a "racemic" dyad, i.

e., successive methyl groups on alternate side of the plane. The percentage of *r* dyads in the chain determines the degree of syndiotacticity of the polymer. Syndiotactic polymers are crystalline and like the isotactic polymers are insoluble in xylene. This crystallinity distinguishes both syndiotactic and isotactic polymers from atactic polymer that is soluble in xylene.

[0033] A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

[0034] The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

Solid Metallocene Catalyst Preparation:

[0035] Methyl aluminoxane supplied as a 10% solution in toluene (density 0.89) was used as the cocatalyst. 40mg of isopropyl (fluorenyl-cyclopentadienyl)zirconium dichloride, was dissolved in 20.0 ml of MAO solution; the solution was stirred and the solvent was removed under high vacuum at room temperature and traces of the remaining solvent were removed with slight warming. The flask was taken into a vacuum Atmospheres dry box; the solid was removed and pulverized to obtain 1.3g purple solid. A known amount of the solid was weighed out and suspended in 2-4 ml of mineral oil (Amoco-10NF), in a Wheaton bottle; shaken thoroughly and injected into a stainless steel sample transfer cylinder as described in the example. Generally, a small amount (estimated to be about 10%) of the solid remained adhered to the glass wall and could not be transferred. It is also likely that small amount of solid remains adhered to the walls of sample transfer cylinder during injection.

EXAMPLE 1

[0036] 10.0 mg of conventional supported Ziegler-Natta catalyst were placed in a stainless steel bomb with 0.2 mmol of cyclohexylmethyldimethoxysilane (CMDs) and 2.0 mmol of triethylaluminum (TEAl). 184 mg of isopropyl(fluorenyl) (cyclopentadienyl)zirconium dichloride/MAO solid were suspended in 4 milliliters of mineral oil. The metallocene/MAO-mineral oil suspension was placed in the bomb. Hydrogen was introduced followed by 1.0 liter of propylene into a 2 liter Zipperclave reactor kept at 60°C. Contents of the bomb were prepolymerized with 0.3 liter of propylene and approximately 16 mmol of hydrogen for 5 seconds at 23°C and then charged into the reactor. The reactor temperature was maintained at 60°C. Polymerization continued for one hour during which time the reactor was maintained at the polymerization temperature. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer yield and analysis is shown in Table I.

EXAMPLE 2 (comparative)

[0037] The procedure of Example 1 was followed except that only the metallocene/MAO of solid (184.0 ml) and TEAl (2.0 mmol) were used in the bomb and hydrogen was omitted. The reactor temperature was initially 20°C and was increased to 60°C after the contents of the bomb were charged to the reactor with 0.3 liter of propylene. The polymer yield and analysis is shown in Table I.

EXAMPLE 3 (comparative)

[0038] The procedure of Example 1 was followed except that the conventional Ziegler-Natta catalyst was not added and the other contents were used in identical quantities.

RUN	TEAL (mmol)	CDS (mmol)	HETEROGENEOUS CATALYST (mg)	METALLOCENE/MAO AMOUNT(mg)	METALLOCENE AMOUNT(mg)	M ₂ (mmol)	TABLE I			TOTAL YIELD (g)	TOLUENE EXTRACT (g)	CATALYST EFFICIENCY (g/g.h)	PER CENT FOULING (%)	BULK DENSITY (g/cc)	T _g (°C)	MAD
							POWDER YIELD (g)	SOLID FOULING (g)	YIELD (g)							
1	2.0	0.2	13.0	184	4	15.7	177	0	177	0	177	n.d. ^{a)}	0	0.40	150 ^{b)}	13.3 ^{c)}
2	2.0	0.0	0.0	184	4	0.0	140	0	140	0	140	35000	0	0.32	135	3.0 ^{d)}
3	2.0	0.2	0.0	184	4	15.7	28	0	28	0	28	7000	0	n.d.	n.d.	

a) n.d. = not determined
b) Small DSC peaks at 126°C and 135°C can be seen due to the presence of syndiotactic polypropylene
c) bimodal distribution; Mw = 421; Mn = 33.0; it is important to note that MAD of IPP obtained under similar conditions in the presence of conventional Ziegler-Natta catalyst system is approximately 8.0.
d) Mw = 57.4x10³; Mn = 18.9x10³

[0039] The standard polymer characterization techniques, namely DSC (Differential Scanning Calorimetry), GPC (Gel Permeation Chromatography) and carbon 13 nuclear magnetic resonance (¹³C NMR) spectroscopy, strongly suggest that the polymer obtained with the mixed catalyst is indeed a blend of syndiotactic and isotactic polypropylene. For example, DSC shows (Figure 1) the presence of two small peaks at approximately 125°C and 135°C corresponding to the melting peaks of syndiotactic polymer obtained with the metallocene and MAO solid. It is also obvious from DSC that isotactic polypropylene is the major component of the blend. GPC teaches that the molecular weight distribution of the polymer is much broader than those obtained when the conventional Ziegler-Natta or metallocene and alumoxane systems separately under the same conditions. Thus for example, the polydispersity of isotactic polypropylene (iPP) obtained with the conventional Ziegler-Natta catalyst used in the present system is approximately 8.0, whereas that of the syndiotactic polypropylene (sPP) obtained with solid MAO and metallocene catalyst used is around 3.0 (Figure 2). However, the polydispersity of the iPP/sPP blend obtained with the mixed catalyst system is 13 (Figure 3). ¹³C NMR (Figure 4) of the polymer provides the most conclusive evidence for the presence of two types of stereoregular polypropylene in the product blend. The mmmm:rrr ratio for the polymer blend product was 77:13 which suggest presence of substantial amounts (>10%) of syndiotactic PP in the predominantly isotactic polymer sample. Generally the isotactic polypropylene polymer obtained with the conventional Ziegler-Natta catalyst contains only traces (<0.5%) of syndiotactic component.

Claims

1. A catalyst system for the polymerization of olefins comprising a combination of at least one homogeneous syndiospecific metallocene catalyst and at least one heterogeneous conventional supported Ziegler-Natta catalyst for producing isotactic polyolefin,
wherein the metallocene catalyst comprises:

a) a neutral metallocene compound of the general formula



wherein (C₅H₄) is a cyclopentadienyl ring and (C₄H_{4-m}R'_mC₅C₄H_{4-n}R'_n) is a fluorenyl ring or a substituted fluorenyl ring wherein (C₅H₄) and (C₄H_{4-m}R'_mC₅C₄H_{4-n}R'_n) have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R* is a structural bridge between the (C₅H₄) and (C₄H_{4-m}R'_mC₅C₄H_{4-n}R'_n) rings to impart stereorigidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; 0 ≤ m ≤ 4; 0 ≤ n ≤ 4; and p is the valence of Me minus 2.

b) an aluminoxane,

wherein the conventional supported Ziegler-Natta catalyst comprises:

- a) a transition metal compound of the general formula MR_x⁺ where M is a Group IIIB, IVB, VB or VIB metal, R⁺ is a halogen or a hydrocarboxyl and x is the valence of the metal and
- b) an aluminum alkyl of the general formula AlR₃[#] where R[#] is an alkyl of from 1-8 carbon atoms and R[#] may be the same or different.

2. A catalyst system as recited in Claim 1 wherein b is 1, R* is a hydrocarbyl radical chosen from the group consisting of an alkylene radical having one to four carbon atoms, a dialkyl germanium, a dialkyl silicon, an alkyl phosphine and an amine radical, M is a Group IVB metal, R' is a halogen or alkyl.
3. A catalyst system as recited in Claim 1 wherein R* is an isopropylene radical.
4. A catalyst system as recited in Claim 1 wherein the aluminoxane is methyl alumoxane.
5. A catalyst system as recited in Claim 1 wherein is a Group IVB, R⁺ is chlorine, bromine, an alkoxy or a phenoxy.
6. A catalyst system as recited in Claim 1 wherein M is titanium and R⁺ is chlorine or ethoxy.

7. A catalyst system as recited in Claim 1 wherein the transition metal compound is chosen from the group consisting of TiCl_4 , TiBr_4 , $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Br}_2$ and $\text{Ti}(\text{OC}_{12}\text{H}_{25})\text{Cl}_3$.
8. A catalyst system as recited in Claim 1 wherein the aluminum alkyl is chosen from the group consisting of trimethyl aluminum, triethyl aluminum and triisobutyl aluminum.
9. A catalyst system as recited in Claim 1 further comprising an electron donor organosilicon compound.
10. A catalyst system as recited in Claim 9 wherein the electron donor is chosen from the group consisting of cyclohexylmethyl dimethoxysilane, diphenyldimethoxysilane and isobutyltrimethoxy silane.
11. A method of making a catalyst system comprising

a) making a homogeneous syndiospecific metallocene catalyst by mixing

1) a neutral metallocene compound of the general formula



wherein (C_5H_4) is a cyclopentadienyl ring and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ is a fluorenyl ring or a substituted fluorenyl ring wherein (C_5H_4) and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R^* is a structural bridge between the (C_5H_4) and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ rings to impart stereoregidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $1 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

2) an aluminoxane,

b) extracting solvent to form a solid complex of the metallocene and the aluminoxane,

c) suspending the solid in mineral oil,

d) making a heterogeneous conventional supported Ziegler-Natta catalyst by separately mixing :

1) a conventional supported Ziegler-Natta catalyst component comprising a transition metal compound of the general formula MR^*_x where M is a Group IIIB, IVB, VB or VIB metal, R^* is a halogen or a hydrocarboxyl and x is the valence of the metal and

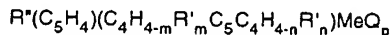
2) an aluminum alkyl of the general formula $\text{AlR}^{\#}_3$ where $\text{R}^{\#}$ is an alkyl of from 1-8 carbon atoms and $\text{R}^{\#}$ may be the same or different,

e) mixing the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst.

12. A process of producing a polymer blend in a single reactor comprising:

a) making a homogeneous syndiospecific metallocene catalyst by

1) selecting a neutral metallocene compound of the general formula



wherein (C_5H_4) is a cyclopentadienyl ring and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ is a fluorenyl ring or a substituted fluorenyl ring wherein (C_5H_4) and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ have bilateral or pseudo-bilateral symmetry; R' is a hydrocarbyl radical having from 1-20 carbon atoms, a halogen, an alkoxy, an alkoxy alkyl or an alkylamino radical, each R' may be the same or different; R^* is a structural bridge between the (C_5H_4) and $(\text{C}_4\text{H}_{4-m}\text{R}'_m\text{C}_5\text{C}_4\text{H}_{4-n}\text{R}'_n)$ rings to impart stereoregidity; Q is a hydrocarbon radical or is a halogen; Me is a Group IIIB, IVB, VB, or VIB metal as positioned in the Periodic Table of Elements; $1 \leq m \leq 4$; $0 \leq n \leq 4$; and p is the valence of Me minus 2.

- 2) adding an aluminoxane to form a syndiospecific metallocene catalyst,
- 3) extracting solvent to form a solid complex of the metallocene and the aluminoxane,
- 4) suspending the solid in mineral oil,

5 b) making a heterogeneous conventional supported Ziegler-Natta catalyst by

- 1) selecting a transition metal compound of the general formula MR^+_x where M is a Group IIIB, IVB, VB or VIB metal, R^+ is a halogen or a hydrocarboxyl and x is the valence of the metal and
- 2) adding an aluminum alkyl of the general formula $AlR^{\#}_3$ where $R^{\#}$ is an alkyl of from 1-8 carbon atoms and $R^{\#}$ may be the same or different to form a conventional supported Ziegler-Natta catalyst

10

15

- c) mixing the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst,
- d) introducing the mixture of the metallocene catalyst in mineral oil and the conventional supported Ziegler-Natta catalyst into a polymerization reaction zone containing a monomer under polymerization conditions, and
- e) withdrawing a polymer product, which is a blend of syndiotactic and isotactic polyolefins.

Patentansprüche

20 1. Katalysatorsystem für die Polymerisation von Olefinen, umfassend eine Kombination von mindestens einem homogenen syndiospezifischen Metallocenkatalysator und mindestens einem heterogenen konventionellen unterstützten Ziegler-Natta Katalysator zum Herstellen von isotaktischem Polyolefin, wobei der Metallocenkatalysator umfaßt:

25 a) eine neutrale Metallocenverbindung der allgemeinen Formel



30 wobei (C_5H_4) ein Cyclopentadienylring ist, und $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ ist ein Fluorenylring oder ein substituierter Fluorenylring, wobei (C_5H_4) und $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ bilaterale oder pseudobilaterale Symmetrie aufweisen; R' ist ein Hydrocarbylrest mit 1-20 Kohlenstoffatomen, ein Halogen-, ein Alkoxy-, ein Alkoxyalkyl- oder ein Alkylaminorest, jedes R' kann gleich oder unterschiedlich sein; R'' ist eine Strukturbrücke zwischen den (C_5H_4) und $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ Ringen zum Verleihen von Stereorigidität; Q ist ein Kohlenwasserstoffrest oder ist ein Halogen; Me ist ein Gruppen IIIB, IVB, VB oder VIB Metall, wie in dem Periodensystem der Elemente angeordnet; $0 \leq m \leq 4$; $0 \leq n \leq 4$; und p ist die Wertigkeit von Me minus 2.

35

b) ein Aluminoxan,

wobei der konventionelle unterstützte Ziegler-Natta-Katalysator umfaßt:

40

- a) eine Übergangsmetallverbindung der allgemeinen Formel MR^+_x , wobei M ein Gruppen IIIB, IVB, VB oder VIB Metall ist, R^+ ein Halogen oder ein Hydrocarboxyl ist, und x die Wertigkeit des Metalls ist, und
- b) ein Aluminiumalkyl der allgemeinen Formel $AlR^{\#}_3$, wobei $R^{\#}$ ein Alkyl mit 1-8 Kohlenstoffatomen ist, und $R^{\#}$ kann gleich oder unterschiedlich sein.

45

2. Katalysatorsystem nach Anspruch 1, wobei b 1 ist, R^+ ist ein Hydrocarbylrest ausgewählt aus der Gruppe bestehend aus einem Alkylrest mit ein bis vier Kohlenstoffatomen, einem Dialkylgermanium, einem Dialkylsilicium, einem Alkylphosfin und einem Aminrest, M ist ein Gruppen IVB Metall, R' ist ein Halogen oder Alkyl.

50

3. Katalysatorsystem nach Anspruch 1, wobei R'' ein Isopropylrest ist.

4. Katalysatorsystem nach Anspruch 1, wobei das Aluminoxan Methylalumoxan ist.

5. Katalysatorsystem nach Anspruch 1, wobei M eine Gruppe IVB ist, R^+ ist Chlor, Brom, ein Alkoxy oder ein Phenoxy.

55

6. Katalysatorsystem nach Anspruch 1, wobei M Titan ist, und R ist Chlor oder Ethoxy.

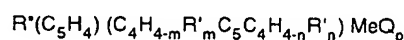
7. Katalysatorsystem nach Anspruch 1, wobei die Übergangsmetallverbindung ausgewählt ist aus der Gruppe be-

stehend aus TiCl_4 , TiBr_4 , $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Br}_2$ und $\text{Ti}(\text{OC}_{12}\text{H}_{25})\text{Cl}_3$.

8. Katalysatorsystem nach Anspruch 1, wobei das Aluminiumalkyl ausgewählt ist aus der Gruppe bestehend aus Trimethylaluminium, Triethylaluminium und Triisobutylaluminium.
9. Katalysatorsystem nach Anspruch 1, ferner umfassend eine Elektronendonorganosiliciumverbindung.
10. Katalysatorsystem nach Anspruch 9, wobei der Elektronendonator ausgewählt ist aus der Gruppe bestehend aus Cyclohexylmethyldimethoxysilan, Diphenyldimethoxysilan und Isobutyltrimethoxysilan.
11. Verfahren zum Herstellen eines Katalysatorsystems, umfassend

a) Herstellen eines homogenen syndiospezifischen Metallocenkatalysators durch Mischen

1) einer neutralen Metallocenverbindung der allgemeinen Formel



wobei (C_5H_4) ein Cyclopentadienylring ist, und $(\text{C}_4\text{H}_4\text{-}_m\text{R}'_m\text{C}_5\text{C}_4\text{H}_4\text{-}_n\text{R}'_n)$ ist ein Fluorenylring oder ein substituierter Fluorenylring, wobei (C_5H_4) und $(\text{C}_4\text{H}_4\text{-}_m\text{R}'_m\text{C}_5\text{C}_4\text{H}_4\text{-}_n\text{R}'_n)$ bilaterale oder pseudobilaterale Symmetrie aufweisen; R' ist ein Hydrocarbylrest mit 1 bis 20 Kohlenstoffatomen, ein Halogen-, ein Alkoxy-, ein Alkoxyalkyl- oder ein Alkylaminorest, jedes R' kann gleich oder unterschiedlich sein; R^* ist eine Strukturbrücke zwischen den (C_5H_4) und $(\text{C}_4\text{H}_4\text{-}_m\text{R}'_m\text{C}_5\text{C}_4\text{H}_4\text{-}_n\text{R}'_n)$ Ringen zum Verleihen von Stereorigidität; Q ist ein Kohlenwasserstoffrest oder ist ein Halogen; Me ist ein Gruppen IIIB, IVB, VB oder VIB Metall, wie in dem Periodensystem der Elemente angeordnet; $1 \leq m \leq 4$; $0 \leq n \leq 4$; und p ist die Wertigkeit von Me minus 2.

2) eines Aluminioxans,

b) Extrahieren von Lösungsmittel unter Bilden eines Feststoffkomplexes des Metallocens und des Aluminioxans,

c) Suspendieren des Feststoffes in Mineralöl,

d) Herstellen eines heterogenen konventionellen unterstützten Ziegler-Natta Katalysators durch getrenntes Mischen:

1) einer konventionellen unterstützten Ziegler-Natta Katalysatorkomponente, umfassend eine Übergangsmetallverbindung der allgemeinen Formel MR^+_x , wobei M ein Gruppen IIIB, IVB, VB oder VIB Metall ist, R^+ ist ein Halogen oder ein Hydrocarboxyl, und x ist die Wertigkeit des Metalls, und

2) eines Aluminiumalkyls der allgemeinen Formel $\text{AlR}^{\#}_3$, wobei $\text{R}^{\#}$ ein Alkyl mit 1 bis 8 Kohlenstoffatomen ist, und $\text{R}^{\#}$ ist ein Alkyl mit 1 bis 8 Kohlenstoffatomen, und $\text{R}^{\#}$ kann gleich oder unterschiedlich sein,

e) Mischen des Metallocenkatalysators in Mineralöl und des konventionellen unterstützten Ziegler-Natta-Katalysators.

12. Verfahren zum Herstellen einer Polymermischung in einem einzelnen Reaktor, umfassend:

a) Herstellen eines homogenen syndiospezifischen Metallocenkatalysators durch

1) Auswählen einer neutralen Metallocenverbindung der allgemeinen Formel



wobei (C_5H_4) ein Cyclopentadienylring ist, und $(\text{C}_4\text{H}_4\text{-}_m\text{R}'_m\text{C}_5\text{C}_4\text{H}_4\text{-}_n\text{R}'_n)$ ist ein Fluorenylring oder ein substituierter Fluorenylring, wobei (C_5H_4) und $(\text{C}_4\text{H}_4\text{-}_m\text{R}'_m\text{C}_5\text{C}_4\text{H}_4\text{-}_n\text{R}'_n)$ bilaterale oder pseudo-bilaterale Symmetrie haben; R' ist ein Hydrocarbylrest mit 1-20 Kohlenstoffatomen, ein Halogen-, ein Alkoxy-, ein Alkoxyalkyl- oder ein Alkylaminorest, jedes R' kann gleich oder unterschiedlich sein; R^* ist eine Struktur-

brücke zwischen den (C_5H_4) und $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ Ringen zum Verleihen von Stereorigidität; Q ist ein Kohlenwasserstoffrest oder ist ein Halogen; Me ist ein Gruppen IIIB, IVB, VB oder VIB Metall, wie in dem Periodensystem der Elemente angeordnet; $1 \leq m \leq 4$; $0 \leq n \leq 4$; und p ist die Wertigkeit von Me minus 2,

- 2) Hinzufügen eines Aluminoxans unter Bilden eines syndiospezifischen Metallocenkatalysators,
- 3) Extrahieren von Lösungsmittel unter Bilden eines Feststoffkomplexes des Metallocens und des Aluminoxans,
- 4) Suspendieren des Feststoffes in Mineralöl,

b) Herstellen eines heterogenen konventionellen unterstützten Ziegler-Natta Katalysators durch

- 1) Auswählen einer Übergangsmetallverbindung der allgemeinen Formel MR^+_x , wobei M ein Gruppen IIIB, IVB, VB oder VIB Metall ist, R^+ ist ein Halogen oder ein Hydrocarboxyl, und x ist die Wertigkeit des Metalls und

- 2) Hinzufügen eines Aluminiumalkyls der allgemeinen Formel AlR^*_3 , wobei R^* ein Alkyl mit 1-8 Kohlenstoffatomen ist, und R^* kann gleich oder unterschiedlich sein, wobei ein konventioneller unterstützter Ziegler-Natta-Katalysator gebildet wird,

c) Mischen des Metallocenkatalysators in Mineralöl und des konventionellen unterstützten Ziegler-Natta-Katalysators,

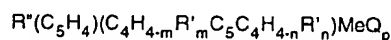
d) Einführen der Mischung des Metallocenkatalysators in Mineralöl und des konventionellen unterstützten Ziegler-Natta-Katalysators in eine Polymerisationsreaktionszone, enthaltend ein Monomer, unter Polymerisationsbedingungen, und

e) Abziehen eines Polymerprodukts, welches eine Mischung aus syndiotaktischen und isotaktischen Polyolefinen ist.

Revendications

1. Système de catalyseurs pour la polymérisation d'oléfines, comprenant une combinaison d'au moins un catalyseur homogène syndiospécifique à base de métallocène et d'au moins un catalyseur hétérogène conventionnel de type Ziegler-Natta déposé sur un support pour obtenir une polyoléfine isotactique, dans lequel le catalyseur à base de métallocène comprend:

a) un composé de métallocène neutre répondant à la formule générale



dans laquelle le groupe (C_5H_4) représente un noyau cyclopentadiényle et le groupe $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ représente un noyau fluorényle ou un noyau fluorényle substitué, dans laquelle le groupe (C_5H_4) et le groupe $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ possèdent une symétrie bilatérale ou pseudobilatérale; R' représente un radical hydrocarbyle contenant de 1 à 20 atomes de carbone, un atome d'halogène, un radical alcoxy, un radical alcoxyalkyle ou un radical alkylamino, chaque radical R' pouvant être identique ou différent; R'' représente un pont de structure entre le noyau (C_5H_4) et le noyau $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ pour conférer une stéréorigidité; Q représente un radical d'hydrocarbure ou représente un atome d'halogène; Me représente un métal du groupe IIIB, du groupe IVB, du groupe VB ou du groupe VIB tels qu'ils sont disposés dans le tableau périodique des éléments; $0 \leq m \leq 4$; $0 \leq n \leq 4$; et p représente la valence de Me moins 2,

b) un aluminoxane;

dans lequel le catalyseur conventionnel de type Ziegler-Natta déposé sur un support comprend:

a) un composé de métal transitoire répondant à la formule générale MR^+_x où M représente un métal du groupe IIIB, IVB, VB ou VIB, R^+ représente un atome d'halogène ou un radical hydrocarbyle et x représente la valence du métal, et

b) un alkylaluminium répondant à la formule générale AlR^*_3 où R^* représente un radical alkyle contenant de 1 à 8 atomes de carbone et R^* peut représenter un radical identique ou différent.

2. Système de catalyseurs selon la revendication 1, dans lequel b représente 1, R* représente un radical hydrocarbyle choisi parmi le groupe constitué par un radical alkylène contenant de 1 à 4 atomes de carbone, par un radical de dialkylgermanium, par un radical de dialkylsilicium, par un radical d'alkylphosphine et par un radical d'amine, M représente un métal du groupe IVB, R' représente un atome d'halogène ou un groupe alkyle.

3. Système de catalyseurs selon la revendication 1, dans lequel R* représente un radical isopropylène.

4. Système de catalyseurs selon la revendication 1, dans lequel l'aluminoxane représente le méthylaluminoxane.

5. Système de catalyseurs selon la revendication 1, dans lequel M représente un métal du groupe IVB, R* représente un atome de chlore, un atome de brome, un groupe alcoxy ou un groupe phénoxy.

6. Système de catalyseurs selon la revendication 1, dans lequel M représente le titane et R* représente un atome de chlore ou un groupe éthoxy.

7. Système de catalyseurs selon la revendication 1, dans lequel le composé de métal transitoire est choisi parmi le groupe constitué par $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)_3Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ et $Ti(OC_{12}H_{25})Cl_3$.

8. Système de catalyseurs selon la revendication 1, dans lequel le radical d'alkylaluminium est choisi parmi le groupe constitué par le triméthylaluminium, le triéthylaluminium et le triisobutylaluminium.

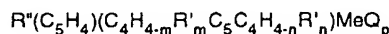
9. Système de catalyseurs selon la revendication 1, comprenant en outre un composé d'organosilicium cédant des électrons.

10. Système de catalyseurs selon la revendication 9, dans lequel le donneur d'électrons est choisi parmi le groupe constitué par le cyclohexylméthyltriméthoxysilane, le diphenyltriméthoxysilane et l'isobutyltriméthoxysilane.

11. Procédé de préparation d'un système de catalyseurs, comprenant le fait de:

a) préparer un catalyseur homogène syndiospécifique à base de métallocène en mélangeant

1) un composé de métallocène neutre répondant à la formule générale



dans laquelle le groupe (C_5H_4) représente un noyau cyclopentadiényle et le groupe $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ représente un noyau fluorényle ou un noyau fluorényle substitué, dans laquelle le groupe (C_5H_4) et le groupe $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ possèdent une symétrie bilatérale ou pseudobilatérale; R' représente un radical hydrocarbyle contenant de 1 à 20 atomes de carbone, un atome d'halogène, un radical alcoxy, un radical alcoxyalkyle ou un radical alkylamino, chaque radical R' pouvant être identique ou différent; R* représente un pont de structure entre le noyau (C_5H_4) et le noyau $(C_4H_4-mR'_mC_5C_4H_4-nR'_n)$ pour conférer une stéréorigidité; Q représente un radical d'hydrocarbure ou représente un atome d'halogène; Me représente un métal du groupe IIIB, du groupe IVB, du groupe VB ou du groupe VIB tels qu'ils sont disposés dans le tableau périodique des éléments; $1 \leq m \leq 4$; $0 \leq n \leq 4$; et p représente la valence de Me moins 2,

2) un aluminoxane;

b) extraire le solvant pour obtenir un complexe du métallocène et de l'aluminoxane sous forme solide;

c) mettre le produit solide en suspension dans de l'huile minérale;

d) préparer un catalyseur hétérogène conventionnel de type Ziegler-Natta déposé sur un support en mélangeant séparément:

1) un composant de catalyseur conventionnel de type Ziegler-Natta déposé sur un support comprenant un composé de métal transitoire répondant à la formule générale MR^*_x où M représente un métal du groupe IIIB, IVB, VB ou VIB, R* représente un atome d'halogène ou un radical hydrocarbyle et x représente la valence du métal, et

EP 0 747 403 B1

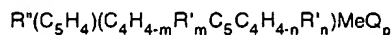
2) un alkylaluminium répondant à la formule générale $AlR^{\#}_3$ où $R^{\#}$ représente un radical alkyle contenant de 1 à 8 atomes de carbone et $R^{\#}$ peut représenter un radical identique ou différent;

e) mélanger le catalyseur à base de métallocène dans de l'huile minérale et le catalyseur conventionnel de type Ziegler-Natta déposé sur un support.

12. Procédé pour préparer un mélange polymère dans un réacteur unique, comprenant le fait de:

a) préparer un catalyseur homogène syndiospécifique à base de métallocène, en passant par les étapes consistant à

1) sélectionner un composé de métallocène neutre répondant à la formule générale



dans laquelle le groupe (C_5H_4) représente un noyau cyclopentadiényle et le groupe $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ représente un noyau fluorényle ou un noyau fluorényle substitué, dans laquelle le groupe (C_5H_4) et le groupe $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ possèdent une symétrie bilatérale ou pseudobilatérale; R' représente un radical hydrocarbyle contenant de 1 à 20 atomes de carbone, un atome d'halogène, un radical alcoxy, un radical alcoxyalkyle ou un radical alkylamino, chaque radical R' pouvant être identique ou différent; $R^{\#}$ représente un pont de structure entre le noyau (C_5H_4) et le noyau $(C_4H_{4-m}R'_mC_5C_4H_{4-n}R'_n)$ pour conférer une stéréorigidité; Q représente un radical d'hydrocarbure ou représente un atome d'halogène; Me représente un métal du groupe IIIB, du groupe IVB, du groupe VB ou du groupe VIB tels qu'ils sont disposés dans le tableau périodique des éléments; $1 \leq m \leq 4$; $0 \leq n \leq 4$; et p représente la valence de Me moins 2,

2) ajouter un aluminosane pour obtenir un catalyseur syndiospécifique à base de métallocène,

3) extraire le solvant pour obtenir un complexe du métallocène et de l'aluminosane sous forme solide,

4) mettre le produit solide en suspension dans de l'huile minérale;

b) préparer un catalyseur hétérogène conventionnel de type Ziegler-Natta déposé sur un support, en passant par les étapes consistant à

1) sélectionner un composé de métal transitoire répondant à la formule générale MR^+_x où M représente un métal du groupe IIIB, IVB, VB ou VIB, R^+ représente un atome d'halogène ou un radical hydrocarbyle et x représente la valence du métal, et

2) ajouter un alkylaluminium répondant à la formule générale $AlR^{\#}_3$ où $R^{\#}$ représente un radical alkyle contenant de 1 à 8 atomes de carbone et $R^{\#}$ peut représenter un radical identique ou différent, pour former un catalyseur conventionnel de type Ziegler-Natta déposé sur un support;

c) mélanger le catalyseur à base de métallocène dans de l'huile minérale et le catalyseur conventionnel de type Ziegler-Natta déposé sur un support;

d) introduire le mélange du catalyseur à base de métallocène dans de l'huile minérale et le catalyseur conventionnel de type Ziegler-Natta déposé sur un support dans une zone réactionnelle de polymérisation contenant un monomère, dans des conditions de polymérisation; et

e) retirer un produit polymère qui représente un mélange homogène de polyoléfines syndiotactiques et isotactiques.

Figure 1. DSC of Polymer Sample from Example 1

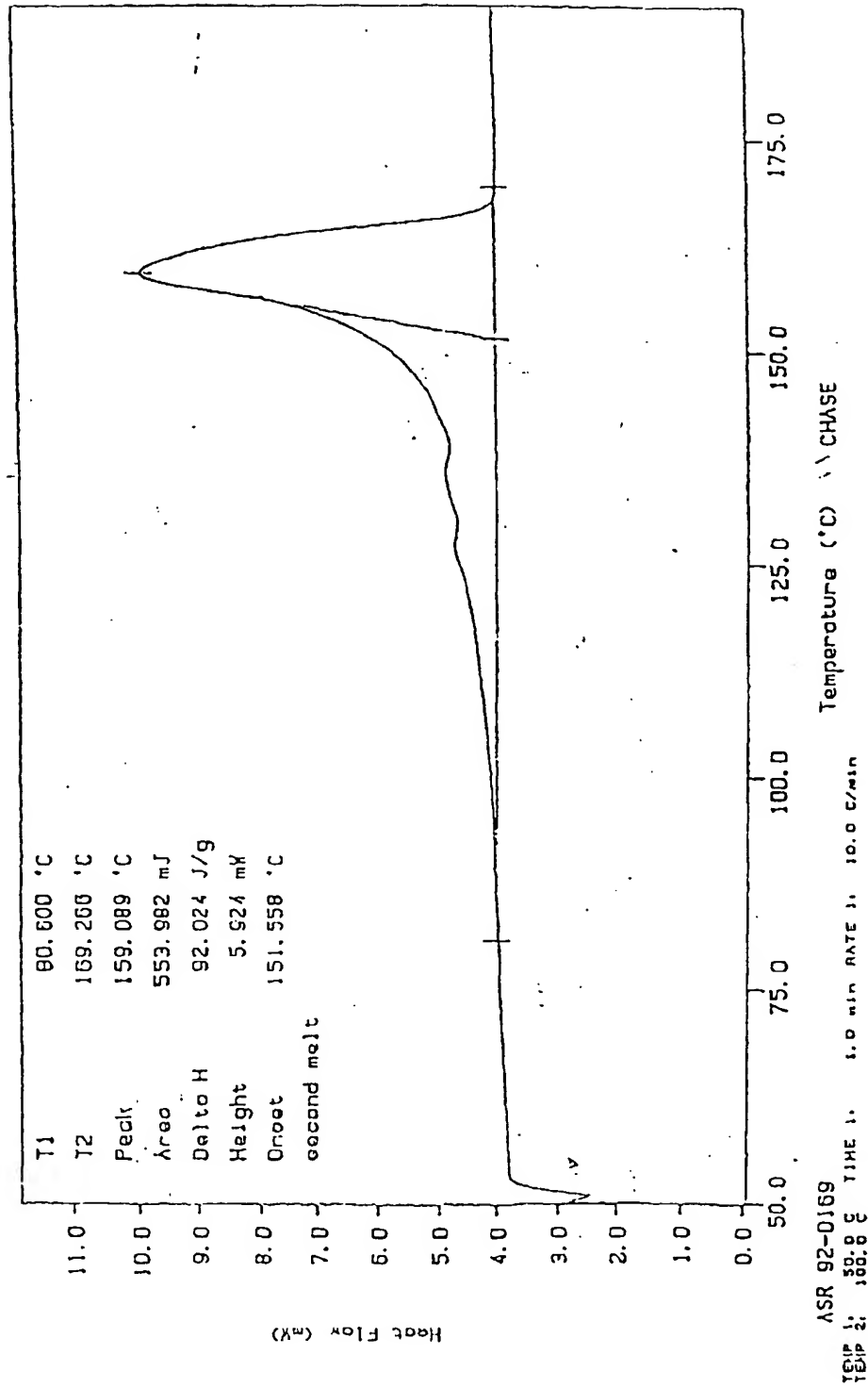
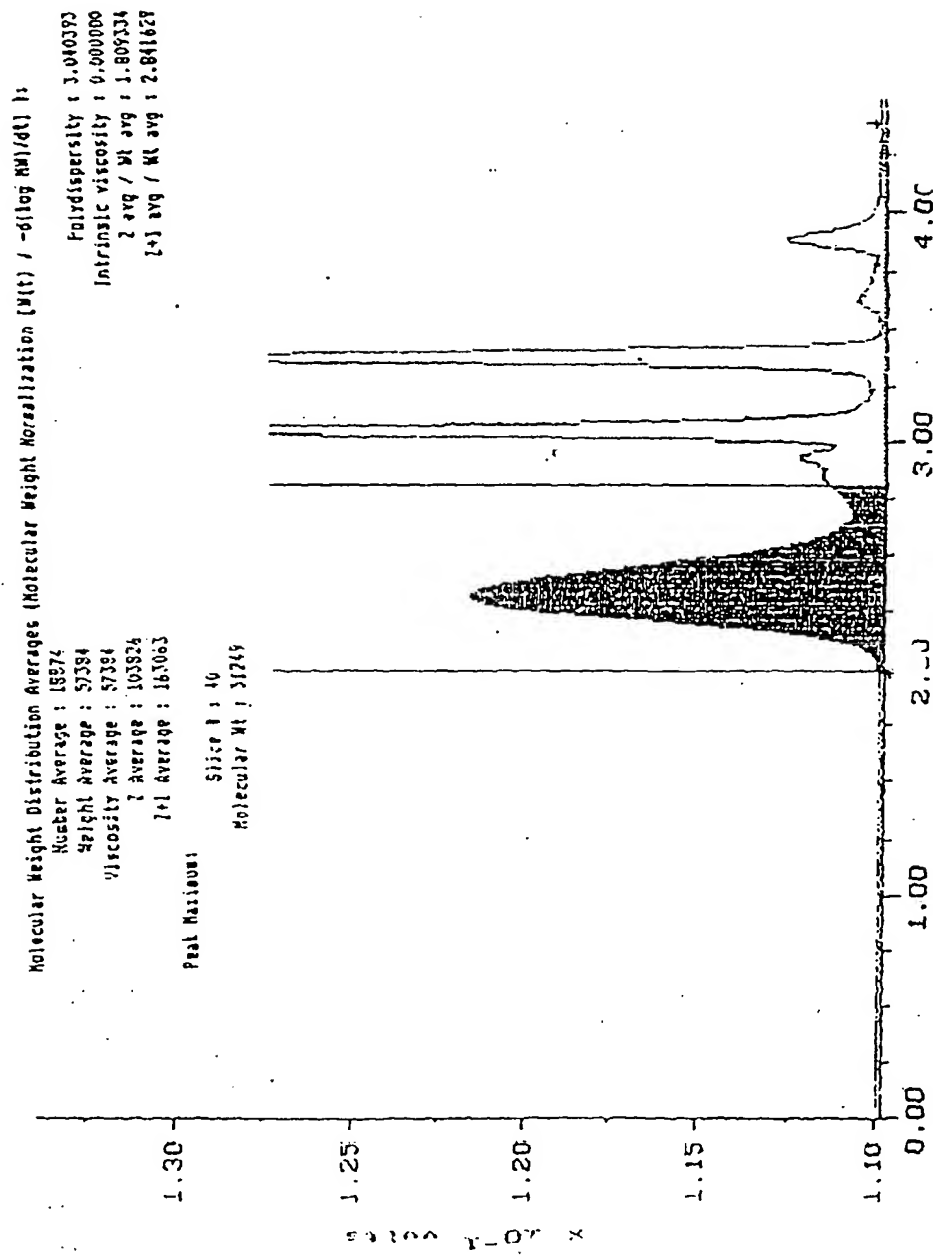
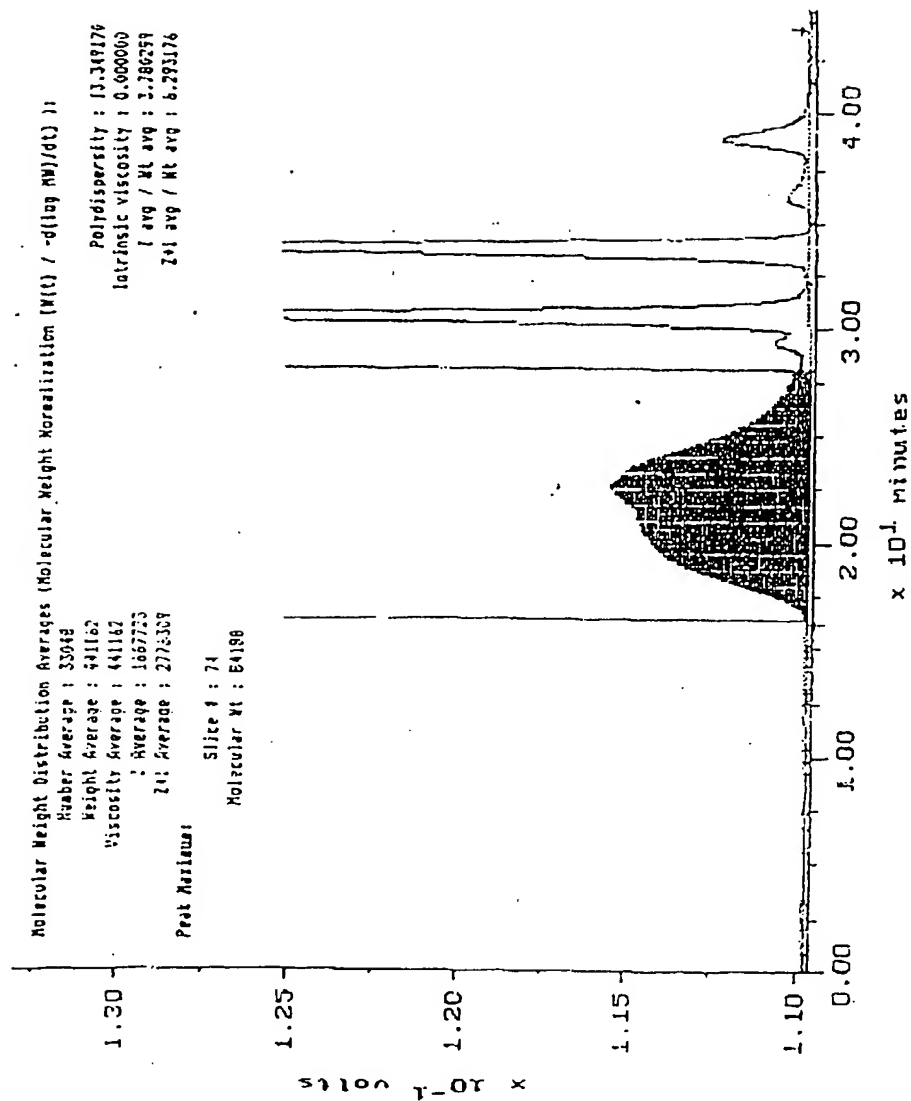


Figure 2. GPC of Polymer Sample from Example 2

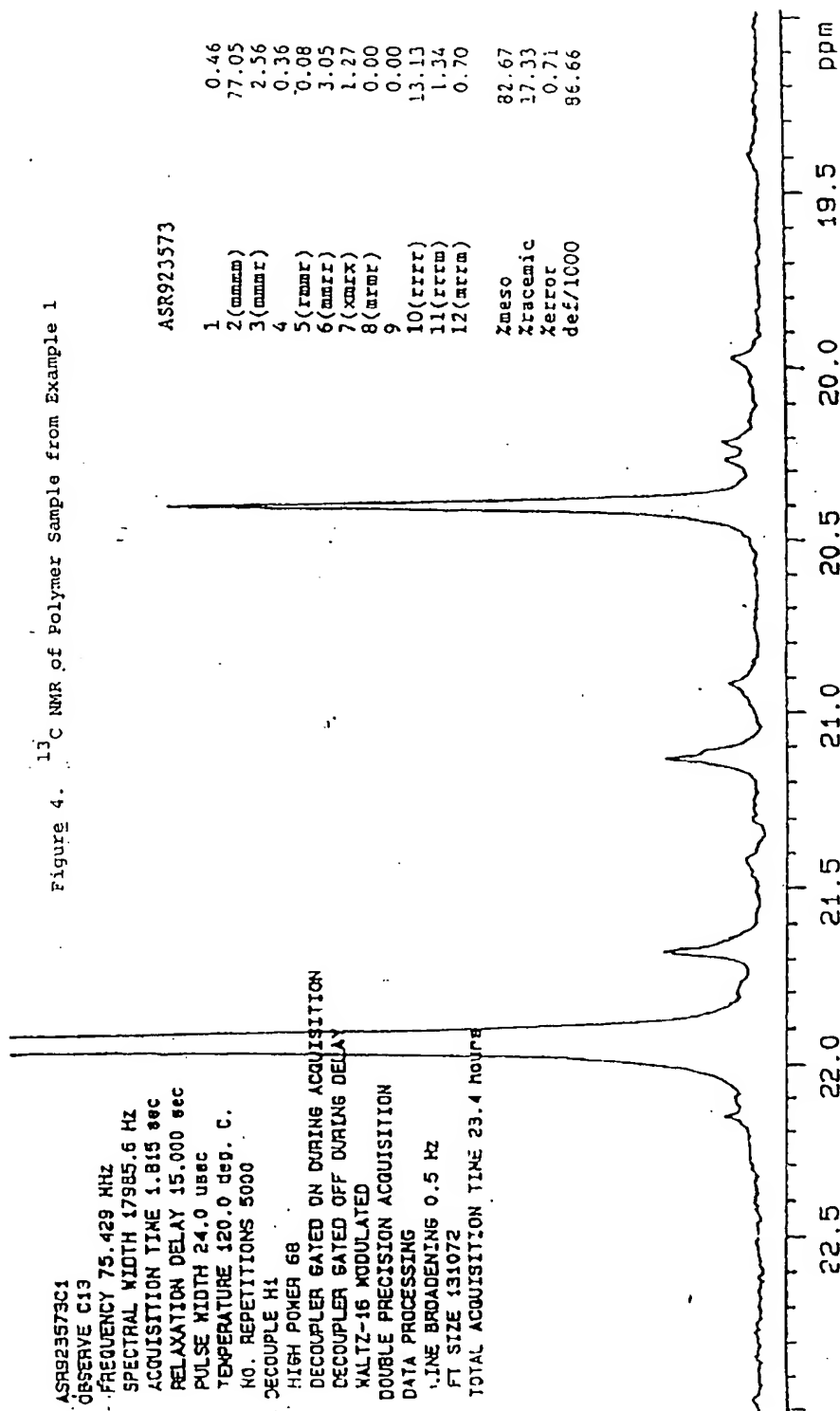


BEST AVAILABLE COPY

Figure 3. GPC of Polymer Sample from Example 1



BEST AVAILABLE COPY

Figure 4. ^{13}C NMR of Polymer Sample from Example 1